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SYNTHESIS OF NEW CALIXARENE-PHOSPHINE OXIDES AND THEIR EXTRACTION PROPERTIES IN IONIC LIQUIDS

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Abstract New calix[4]arenes functionalized by $\text{Alk}_2\text{P}(\text{O})\text{CH}_2$ binding groups and *N*-methylimidazolium groups at the opposite rims of the macrocyclic skeleton have been synthesized and characterized. Their extraction properties towards of Eu^{3+} and Am^{3+} in ionic liquid were investigated.

Keywords Calixarenes; ionic liquids; phosphine oxides

INTRODUCTION

The use of nuclear power has led to the accumulation of great amounts of both high- and medium-level activity radioactive wastes, which require efficient methods of separation and safe disposal. The main method for the decontamination of radioactive wastes is liquid–liquid extraction of hazardous radionuclides followed by burial or transmutation. A modern approach in the design of efficient and selective extractants of radionuclides is based on the functionalization of calixarene platform by several $\text{P}=\text{O}$ containing fragments, capable of cooperatively binding metal cations.¹ Room temperature ionic liquids (RTIL) are promising solutions for the extraction of the radionuclides from spent nuclear fuel.²

RESULTS AND DISCUSSION

We present in this article the synthesis of a series of new *cone*-shaped calix[4]arenes possessing $\text{CH}_2\text{P}(\text{O})\text{Alk}_2$ metallocomplexing groups at the macrocyclic wide and narrow rim and *N*-methylimidazolium groups at the narrow rim. Extraction properties of the calixarene synthesized and dissolved in ionic liquid were investigated.

Calix[4]arenes **3–10** functionalized by four or eight $\text{Alk}_2\text{P}(\text{O})\text{CH}_2$ binding groups have been synthesized by the Arbuzov reaction of tetrachloromethylcalix[4]arenes **1, 2** with dialkylphosphinites.

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Figure 1 Synthesis of calixarene phosphine oxides.

Figure 2 Extraction of Eu^{3+} , UO_2^{2+} , Am^{3+} by phosphine oxides from HNO_3 (0.3M) into *N*-butyl-*N*-methylimidazolium $\times$ Tf_2N . D—distribution ratio of the metal cations between the ionic liquid and HNO_3 phases; TAPO—triocetylphosphine oxide.

30 Tetra(*N*-methylimidazolium) derivatives **11**, **12** were prepared by the reaction of
31 bromobutoxycalixarenes **8**, **10** with *N*-methylimidazole. Metathetical reactions of bromides
32 **11**, **12** with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in DMF gave new quaternary salts **13**, **14** (Figure 1).

33 Extraction properties of some calixarene phosphine oxides towards of Eu^{3+} , UO_2^{2+} ,
34 and Am^{3+} were investigated in ionic liquid *N*-butyl-*N*-methylimidazolium $\times$ Tf_2N (Figure
35 2). The calixarene tetrphosphine oxides **5–7** are more efficient extractants than industrial
36 trialkylphosphine oxides. Calixarene **5** demonstrates high selectivity in UO_2^{2+} extraction.

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